AN ATTEMPT AT OPTIMIZING THE FLOW CHARACTERISTICS OF BLAST FURNACE SLAG BY INVESTIGATION WITH SYNTHETIC SLAG PREPARED IN THE LABORATORY USING PURE OXIDES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENT FOR THE DEGREE OF

Bachelor of Technology
in
Metallurgical and Materials Engineering

By

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CERTIFICATE

This is to certify that the thesis entitled, "**An attempt at optimising the flow characteristics of Blast Funace Slag by investigation with synthetic slag prepared in the laboratory**" submitted by **Deepak Nayak (10604042), Himansu Shekhar Mahapatra (10604039) and Navin Kumar (10604014)**, in partial fulfillments for the requirements for the award of **Bachelor of Technology Degree** in **Metallurgical and Materials Engineering** at National Institute of Technology, Rourkela is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ABSTRACT

In the cohesive zone the ore layer becomes compacted due to softening-melting and the gas passes predominantly through the sandwiched coke layer (coke slits). Minimizing the size and lowering the position of the cohesive zone will improve productivity and decrease coke rate. This work is designed at arriving at a slag composition through actual experimentations which will ensure the lowering of the cohesive zone of the blast furnace with simultaneous decrease in the difference between the softening temperature (ST) and flow temperature (FT) of the slag. Slag samples from SAIL, Rourkela were brought and their flow characteristics were measured under the heating microscope. With the same composition as obtained from the plant, a synthetic slag was prepared in the laboratory. It was melted to 1600 °C and then water quenched to form the glassy state. Flow characteristics for the same were also determined. In addition, all slag samples were sent to DISIR, Rajgangpur for slag analysis as well as to determine the mineralogical phases present in them. For this, they heated the slag samples to 1500 °C followed by slow cooling to convert them to crystalline form. Then, XRD analysis was done to determine the mineralogical phases. Finally, with relevant phase diagram study, we arrived at a composition which will ensure the lowering of cohesive zone. Moreover, flow characteristics data of synthetic slag was compared with that obtained from Blast Furnace slag.

CONTENTS

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

The characteristic behavior of a slag under any operating conditions is a function of its composition and the various constituents present in it of which the fluxing constituents are the most important ones. It is in this context that an attempt has been made at arriving at a slag composition through actual experimentations with synthetic slag which will ensure the lowering of the cohesive zone of the blast furnace with simultaneous decrease in the difference between the softening temperature (ST) and flow temperature (FT) of the slag. We have borrowed the flow characteristics data of Blast Furnace Slag to have a comparison with that of synthetic slag.

Slag making has always been a part of steel and iron making. After all, at least 10% of what is produced in the steel and iron making process is slag. In ancient times, the secret to steel and iron making was in the slag formulations. Today's iron maker has a better understanding of the importance of blast furnace slag compositions and their affects on hot metal economics and quality. There is an old saying in iron making "Take care of the slag and it will take care of the metal". Slags are an important part of making hot metal quality. They remove unwanted oxides, sulphides, nitrides and phosphides. However slag compositions must be closely controlled or else they will cause additional problems and become liabilities. Improper slag compositions can lead to harmful reversion of S, P, Si and various oxide inclusions.

In order that a blast furnace slag is practicable and most effective, it must be a completely homogenous liquid at the operating temperatures. It must be also have sufficient fluidity so that it can run out of the hearth freely without any loss of production time. In addition to it the slag must ensure

- removal of impurities
- best possible slag-metal reaction
- less metal entrapment through better slag-metal separation.

In blast furnace, formation of slag and the mineralogical transformation that the slag undergoes during descend of burden inside the furnace; influence the quality of hot metal. It is known that the components of slag namely silica and alumina increase the viscosity whereas the presence of calcium oxide reduces the viscosity. The melting zone of slag determines the cohesive zone of blast furnace and hence the fluidity and melting characteristics of slag play a major role in determining the blast furnace productivity. Initially iron rich slag is formed and thereafter due to assimilation of CaO and MgO from flux, the composition of slag varies. As the slag trickles down, it assimilates silica and alumina of ash, generated from combustion of coke. The process of trickling down depends on viscosity of slag, which further is governed by the composition and temperature of the melt.

The shape and position of the cohesive zone in the blast furnace affect the gas flow pattern, which has an effect on the efficiency and productivity of the process. This zone is the region where the metallic burden loses its permeability, and gas flow occurs only through the coke layers. In the cohesive zone, different phenomena occur at the same time, the softening and melting of the oxide phase and the softening and melting of the metallic iron phase. The slag generated from a pyrometallurgical process should have a low fusion-temperature so that at the furnace operating temperature a high available super-heat will increase the kinetics of chemical reactions and will ensure better slag–metal separation. It is in this context that many investigations have been carried out in the past to study the effect of compositional variations on liquidus temperature. However, behaviour of a single constituent in a multi-component slag is different in different circumstances due to its interaction with other constituents. Hence it is essential to study the liquidus temperature of each particular slag resulting from a specific process.

The liquidus temperature has been reported by various nomenclatures by various investigators. Osborn [1] and Snow [2] reported liquidus temperature as the temperature at which the first crystal forms during cooling down the melt whereas Ohno *et al.* [3] reported it as the temperature at which the last crystal disappears during heating. The liquidus temperature or fusion point in German Industrial Standards 51730 has been defined as the hemispherical temperature, i.e., the temperature at which a small mass of the slag assumes the shape of a hemisphere on heating. The heating microscope method is adopted to measure this hemispherical temperature.

In industrial melts, i.e., when a pyrometallurgical process is carried out in a furnace, it is the fusion behaviour of the non-metallic melts (i.e., the mixture of oxides which would combine to make the slag) which is more important than the exact fusion temperature. The fusion behaviour is described in terms of four characteristic temperatures. These are; the initial deformation temperature (IDT) symbolising the surface stickiness; the softening temperature (ST), symbolizing the plastic distortion; the hemispherical temperature (HT), which is also the liquidus temperature, symbolising sluggish flow; and the flow temperature (FT), symbolising liquid mobility. The fusion behaviour of the slag is very relevant in smelting and refining processes. The IDT, indicating the surface stickiness of the material is important for movement of the material in the solid state. Similarly the ST, which indicates the start of plastic distortion along with the HT which represents the fusion or liquidus temperature of the material, plays a significant role in the aerodynamics and heat and mass transfer. In a Blast furnace, for example, a high softening and a high fusion temperature of iron bearing materials would lower the cohesive (softening-melting) zone in the furnace thus decreasing the distance travelled by the molten metal droplets in the furnace there by decreasing the silicon pick-up. [4]

1.1. BLAST FURNACE

The purpose of a blast furnace is to chemically reduce and physically convert iron oxides into liquid iron called "hot metal". The blast furnace is a huge, steel stack lined with refractory brick, where iron ore, coke and limestone are dumped into the top, and preheated air is blown into the bottom. The raw materials require 6 to 8 hours to descend to the bottom of the furnace where they become the final product of liquid slag and liquid iron. These liquid products are drained from the furnace at regular intervals. The hot air that was blown into the bottom of the furnace ascends to the top in 6 to 8 seconds after going through numerous chemical reactions. Once a blast furnace is started it will continuously run for four to ten years with only short stops to perform planned maintenance.

1.2. BLAST FURNACE PROCESS

Iron oxides can come to the blast furnace plant in the form of raw ore, pellets or sinter. The raw ore is removed from the earth and sized into pieces that range from 0.5 to 1.5 inches. This ore is either Hematite (Fe_2O_3) or Magnetite (Fe_3O_4) and the iron content ranges from 50% to 70%. This iron rich ore can be charged directly into a blast furnace without any further processing. Iron ore that contains a lower iron content must be processed or beneficiated to increase its iron content. Pellets are produced from this lower iron content ore. This ore is crushed and ground into a powder so the waste material called gangue can be removed. The remaining iron-rich powder is rolled into balls and fired in a furnace to produce strong, marble-sized pellets that contain 60% to 65% iron. Sinter is produced from fine raw ore, small coke, sand-sized limestone and numerous other steel plant waste materials that contain some iron. These fine materials are proportioned to obtain desired product chemistry then mixed together. This raw material mix is then placed on a sintering strand, which is similar to a steel conveyor belt, where it is ignited by gas fired furnace and fused by the heat from the coke fines into larger size pieces that are from 0.5 to 2.0 inches. The iron ore, pellets and sinter then become the liquid iron produced in the blast furnace with any of their remaining impurities going to the liquid slag.

The coke is produced from a mixture of coals. The coal is crushed and ground into a powder and then charged into an oven. As the oven is heated the coal is cooked so most of the volatile matter such as oil and tar are removed. The cooked coal, called coke, is removed from the oven after 18 to 24 hours of reaction time. The coke is cooled and screened into pieces ranging from one inch to four inches. The coke contains 90 to 93% carbon, some ash and sulfur but compared to raw coal is very strong. The strong pieces of coke with a high energy value provide permeability, heat and gases which are required to reduce and melt the iron ore, pellets and sinter.

The final raw material in the iron making process is limestone. The limestone is removed from the earth by blasting with explosives. It is then crushed and screened to a size that ranges from 0.5

inch to 1.5 inch to become blast furnace flux. This flux can be pure high calcium limestone, dolomite limestone containing magnesia or a blend of the two types of limestone.

Since the limestone is melted to become the slag which removes sulfur and other impurities, the blast furnace operator may blend the different stones to produce the desired slag chemistry and create optimum slag properties such as a low melting point and a high fluidity.

All of the raw materials are stored in an ore field and transferred to the stock house before charging. Once these materials are charged into the furnace top, they go through numerous chemical and physical reactions while descending to the bottom of the furnace.

The iron ore, pellets and sinter are reduced which simply means the oxygen in the iron oxides is removed by a series of chemical reactions. These reactions occur as follows:

- Begins at 850^0 F

$$3Fe_2O_3 + CO = CO_2 + 2Fe_3O_4$$

- Begins at 1100° F

$$Fe_3O_4 + CO = CO_2 + 3FeO$$

- Begins at 1300° F

$$FeO + CO = CO_2 + Fe$$

or

$$FeO + C = CO + Fe$$

At the same time the iron oxides are going through these purifying reactions, they are also beginning to soften then melt and finally trickle as liquid iron through the coke to the bottom of the furnace.

The coke descends to the bottom of the furnace to the level where the preheated air or hot blast enters the blast furnace. The coke is ignited by this hot blast and immediately reacts to generate heat as follows:

$$C + O_2 = CO_2 + \text{Heat}$$

Since the reaction takes place in the presence of excess carbon at a high temperature the carbon dioxide is reduced to carbon monoxide as follows:

$$CO_2 + C = 2CO$$

The product of this reaction, carbon monoxide, is necessary to reduce the iron ore as seen in the previous iron oxide reactions.

The limestone descends in the blast furnace and remains a solid while going through its first reaction as follows:

$$CaCO_3 = CaO + CO_2$$

This reaction requires energy and starts at about 1600°F. The CaO formed from this reaction is used to remove sulfur from the iron which is necessary before the hot metal becomes steel. This sulfur removing reaction is:

$$FeS + CaO + C = CaS + FeO + CO$$

The CaS becomes part of the slag. The slag is also formed from any remaining Silica (SiO_2), Alumina (Al_2O_3), Magnesia (MgO) or Calcia (CaO) that entered with the iron ore, pellets, sinter or coke. The liquid slag then trickles through the coke bed to the bottom of the furnace where it floats on top of the liquid iron since it is less dense.

Another product of the ironmaking process, in addition to molten iron and slag, is hot dirty gases. These gases exit the top of the blast furnace and proceed through gas cleaning equipment where particulate matter is removed from the gas and the gas is cooled. This gas has a considerable energy value so it is burned as a fuel in the "hot blast stoves" which are used to preheat the air entering the blast furnace to become "hot blast". Any of the gas not burned in the stoves is sent to the boiler house and is used to generate steam which turns a turbo blower that generates the compressed air known as "cold blast" that comes to the stoves.

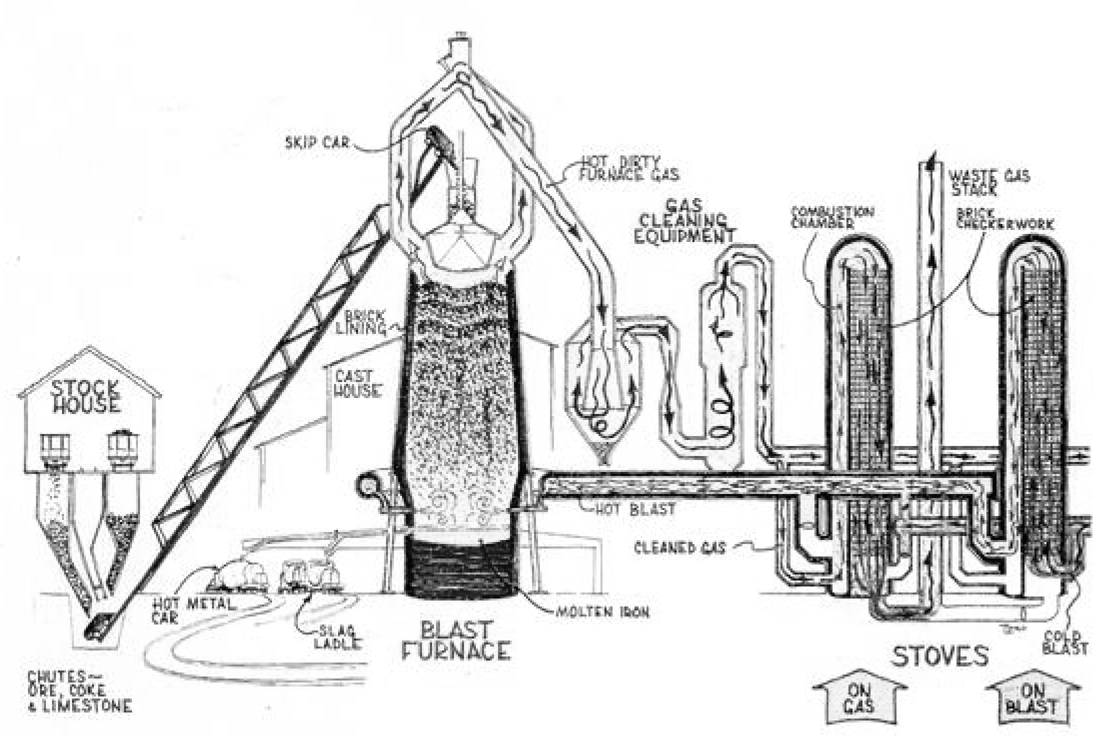


Fig. 1-A sketch showing Blast Furnace Process

In summary, the blast furnace is a counter-current realtor where solids descend and gases ascend. In this reactor there are numerous chemical and physical reactions that produce the desired final product which is hot metal. Typical hot metal chemistry follows: [5]

Iron (Fe) = 93.5-95.0%
Silicon (Si) = 0.30-0.90%
Sulfur (S) = 0.025-0.050%
Manganese (Mn) = 0.55-0.75%
Phosphorous (P) = 0.03-0.09%
Titanium (Ti) = 0.02-0.06%
Carbon (C) = 4.1-4.4%

1.3. BLAST FURNACE REACTIONS

The reduction and smelting of iron ore is done mainly in the iron blast furnace. The burden charged at the top of the furnace consists primarily of iron ore, flux and coke. The reducing gas carbon monoxide and the heat required for the smelting of the ore are generated at the bottom of the furnace by blowing preheated air into the coke bed. The slag and metal accumulate as two liquid layers at the bottom of the furnace. In order that efficient conversion occurs of reactants to products there is an overall chemical stoichiometry which must be met. In addition, specific thermal requirements must also be satisfied to permit the endothermic reactions to proceed and the products brought to their final temperatures. The blast furnace can be conveniently divided into three zones for a study of the physical and chemical reactions occurring therein. These zones are as follows:

- The upper or pre-heating or preparation zone.
- The middle or indirect reduction or thermal reserve or isothermal zone.
- The lower or processing or melting or direct reduction zone.

1.3.1. REACTIONS IN THE UPPER ZONE

The reactions of primary concern in the iron blast furnaces are the reduction reactions of iron oxides. The formation of product layers during the reduction of iron ore is well known. The greater the driving forces for reduction and the faster the rate of chemical reaction, the more pronounced is the formation of the product layers. There is general agreement that the reaction is first order relative to the partial pressure of the reacting gas.

$$3\ Fe_2O_3 + CO = CO_2 + 2\ Fe_3O_4 + 10.33\text{kcal} \qquad (1)$$

$$Fe_3O_4 + CO = CO_2 + 3\ FeO - 8.75\text{kcal} \qquad (2)$$

$$FeO + CO = CO_2 + Fe + 3.99\text{kcal} \qquad (3)$$

At the same time the iron oxides are going through these purifying reactions, they are also beginning to soften then melt and finally trickle as liquid iron through the coke to the bottom of the furnace. Magnetite is reduced to wustite mainly at 700-900° C, thermodynamically carbon deposition from CO by the reaction

$$2CO = CO_2 + C + 41.21\text{kcal} \qquad (4)$$

The deposition occurs predominantly in a narrow temperature range 440-600° C, the presence of iron and its oxides catalyses the reaction. It is also possible for CO to reduce H_2O in the upper furnace to a certain extent

$CO + H_2O = CO_2 + H_2 + 9.68Kcal$ (5)

The decomposition of carbonates other than those of calcium occurs at a relatively low temperature around 400° C. They are of very little importance because modern furnaces are using pellets or sinter and these carbonates are calcined outside.

1.3.2. REACTIONS IN THE MIDDLE ZONE

It is a moderate temperature zone where the temperature ranges between 800-1000° C. Most of the indirect reduction of wustite (Eq. 3) occurs in this zone. The CO/CO_2 ratio of the gas in the inactive zone is about 2.3, a value exhibiting equilibrium with Fe-FeO (Eq. 3). The larger the height of the 800-1000° C temperature zone the longer the gas/solid contact time at these temperature and the greater the degree of indirect reduction. Similarly, the higher the reducibility of the ore the more rapid is the reduction. In short the rate of reduction of ore in the middle zone must not be a restriction for the attainment of optimum coke rate.

1.3.3. REACTIONS IN THE LOWER ZONE

The temperature of the lower zone is 900-1000° C. A variety of physical and chemical processes occurs in this zone. Most of the unreduced iron oxides descends into the lower zone as fayalite, calcium ferrites or intermixed in the primary slag. Direct reduction of iron oxide proceeds at temperatures above 1000 ° C according to:

$FeO + CO = Fe + CO_2$ (6)

$C + CO_2 = 2CO$

The reduction of Si and Ti require very high temperatures while the oxides of Ca, Mg and Al are so stable that they are reduced to a very negligible extent. The reduction of Mn from its monoxide is much more difficult and occurs at a still higher temperature. The extent of reduction varies with temperature and slag basicity. Cr and V behave in the same way as Mn.

$MnO + C = Mn + CO$ (7)

$SiO_2 + 2C = Si + 2CO$ (8)

$S + CaO + C = CaS + CO$ (9)

A major portion of P is present as tri- or tetra- phosphate of Ca. Silica helps in breaking phosphate bond. [6]

$3CaO.P_2O_5 + 3SiO_2 = 3(CaO.SiO_2) + P_2O_5$ (10)

$P_2O_5 + 5C = 2P + 5CO$ (11)

1.4. DIFFERENT ZONES OF BLAST FURNACE

The practical significance of softening and melting characteristics on blast furnace operation was conclusively established in seventies by data obtained from dissection of several quenched commercial blast furnace in Japan. The dissection studies revolutionized the understanding of blast furnace process by providing detail accounts of physical and chemical phenomenon in the blast furnace. It was found that the internal state of a blast furnace consisted of five distinctly different yet highly interrelated zones. These are:

- Granular zone/isothermal zone
- Cohesive zone
- Active coke zone
- Stagnant coke zone
- Hearth

And perhaps the single most important finding of the dissection studies was the existence of the cohesive zone, in the approximate temperature range 1000-1500^{o}C.

The shape and location of this zone had a profound impact on blast furnace productivity, fuel consumption, hot metal quality, operational stability and lining life. The configuration of the cohesive zone found to be a function of iron bearing material properties. The softening and melting characteristics of the iron bearing material were considered to be important to this respect. This provides a great for analyzing softening and melting phenomena.

1.4.1. COHESIVE ZONE

Cohesive zone is a region in blast furnace, where softening and melting of burden materials takes place. It is also the zone where most of the solid volume disappears driving the solid flow. The position of cohesive zone and thickness of cohesive zone are the two factors which decide the performance of a blast furnace. The things affected by the position and thickness of cohesive zone are as follows:

- Gas permeability
- Extent of indirect reduction of wustite
- Silicon content of the liquid pig iron

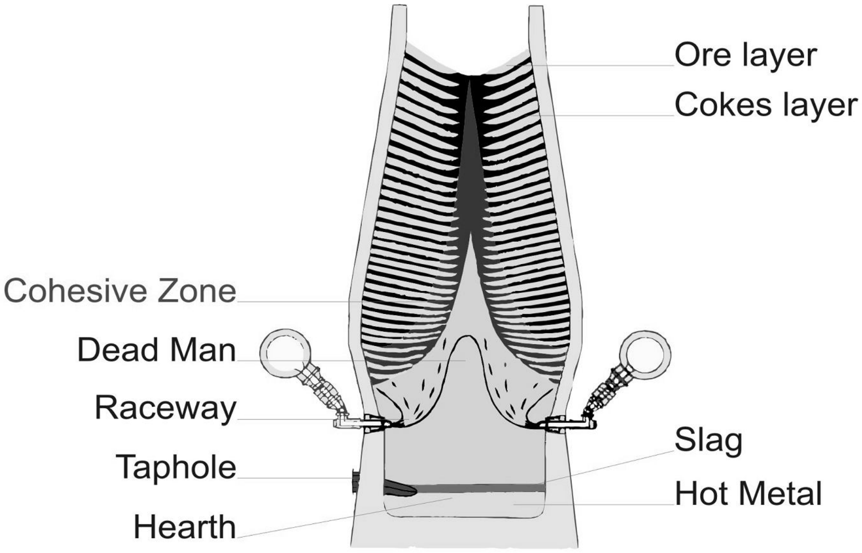


Fig. 2-Cohesive Zone [7]

1.4.1.1. GAS PERMEABILITY

Gas permeability deals with thickness of cohesive zones. Cohesive zones have alternative impermeable, semi fluid layers which resist the flow of ascending gases.

If the thickness of cohesive zones is less, then more and more gases are allowed to pass through, under a given pressure difference, owing to the short length of coke slit. However, the wind volume depends not only on the length of coke slit, but also on the viscosity band volume of the melt and their resulting influence on bed permeability.

1.4.1.2. EXTENT OF INDIRECT REDUCTION

It depends on the position of the cohesive zone. If the cohesive zone is positioned deeper into the blast furnace, the volume of the granular zone is increased, and the descending materials spend more time in the granular zone. So the ascending carbon monoxide gas is utilized in a better way to reduce the wustite indirectly. That is, the extent of indirect reduction is increased in a relatively lower positioned cohesive zone and coke consumption for the production of 1tonne of pig iron is decreased.

1.4.1.3. Si CONTENT OF PIG IRON

Si content in pig iron is mainly due to the reduction of SiO produced by reduction of SiO_2, present in ash after burning of coke near the raceway. SiO reduction takes place in the dripping zone or bosh region.

So by lowering the position of the cohesive zone into the blast furnace, the volume of dripping zone is reduced and SiO gets less chance to reduce and consequently the Si content in the pig iron is decreased.

$$SiO_2 + C = SiO + CO$$

$$[Fe] + SiO = [Si] + (FeO)$$

$$(FeO) + CO = [Fe] + CO_2$$

$$C + CO_2 = 2CO$$

1.5. BLAST FURNACE SLAG

1.5.1. ORIGIN

In the production of iron, iron ore, iron scrap, and fluxes (limestone and/or dolomite) are charged into a blast furnace along with coke for fuel. The coke is combusted to produce carbon monoxide, which reduces the iron ore to a molten iron product. This molten iron product can be cast into iron products, but is most often used as a feedstock for steel production.

Blast furnace slag is a nonmetallic co product produced in the process. It consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates. The molten slag, which absorbs much of the sulfur from the charge, comprises about 20 percent by mass of iron production. **Fig. 3** represents a general schematic of blast furnace operation which depicts the blast furnace feed stocks and the production of blast furnace co products (iron and slag). [8]

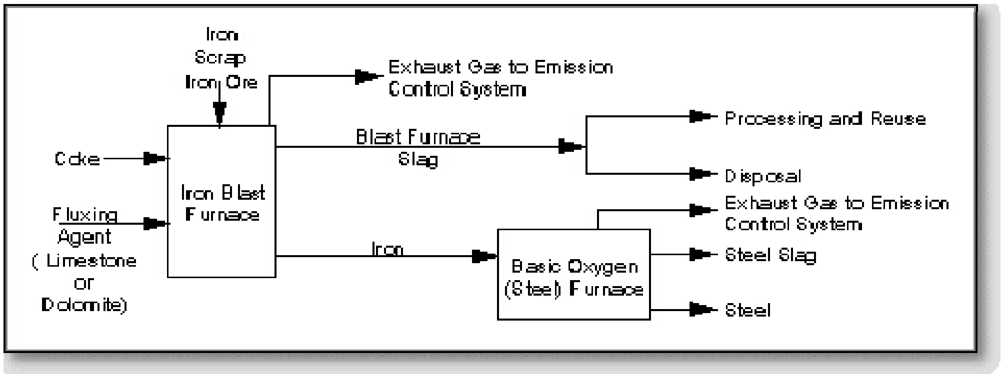


Fig. 3-General schematic of blast furnace operation and blast furnace slag production

1.5.2. FORMS OF SLAG

- **Air-Cooled Blast Furnace Slag**

If the liquid slag is poured into beds and slowly cooled under ambient conditions, a crystalline structure is formed, and a hard, lump slag is produced, which can subsequently be crushed and screened.

- **Expanded or Foamed Blast Furnace Slag**

If the molten slag is cooled and solidified by adding controlled quantities of water, air, or steam, the process of cooling and solidification can be accelerated, increasing the cellular nature of the slag and producing a lightweight expanded or foamed product. Foamed slag is distinguishable from air-cooled blast furnace slag by its relatively high porosity and low bulk density.

- **Pelletized Blast Furnace Slag**

A variation of granulating in which less water is used with violent impelling of the viscous, but rapidly cooling slag through the air. By controlling the process, the pellets can be made more crystalline, which is beneficial for aggregate use, or more vitrified (glassy), which is more desirable in cementitious applications.

- **Granulated Blast Furnace Slag**

If the molten slag is cooled and solidified by rapid water quenching to a glassy state, little or no crystallization occurs. This process results in the formation of sand size (or frit-like) fragments, usually with some friable clinkerlike material. The physical structure and gradation of granulated slag depend on the chemical composition of the slag, its temperature at the time of water quenching, and the method of production. When crushed or milled to very fine cement-sized particles, ground granulated blast furnace slag (GGBFS) has cementitious properties, which make a suitable partial replacement for or additive to Portland cement.

1.5.3. BLAST FURNACE SLAG STRUCTURE

Liquid slags are homogenous melts consisting of oxides of silicon and other elements. They are known to possess electrical properties and consist of simple and complex ions. Crystal analysis of solid silica shows that silicon occupies the centre of a tetrahedron surrounded by 4 oxygen atoms, one at each of the four corners. Each oxygen atom is bonded to two silicon atoms and the network is continuous in three dimensions. These tetrahedral can share only corners so that when every corner oxygen atom is shared, the substance formed will have an overall stoichiometric formula of SiO_2. A Si atom has 4 charges. As each oxygen atom of the tetrahedron has a residual valency, therefore, the SiO_4 group carries 4 negative charges, i.e. $(SiO_4)^{4-}$.

In the crystalline state the tetrahedral arrangement of the silicon and oxygen atoms is symmetrical. The solid structure does not undergo any sudden change on fusion, as expected. In molten or vitreous silica the structure becomes distorted but most of the corners remain shared. The viscosity of molten silica is very high ($\approx 10^5$ P), the corners being linked tightly in all directions in a vast network. These are apparent from **Fig. 4.**

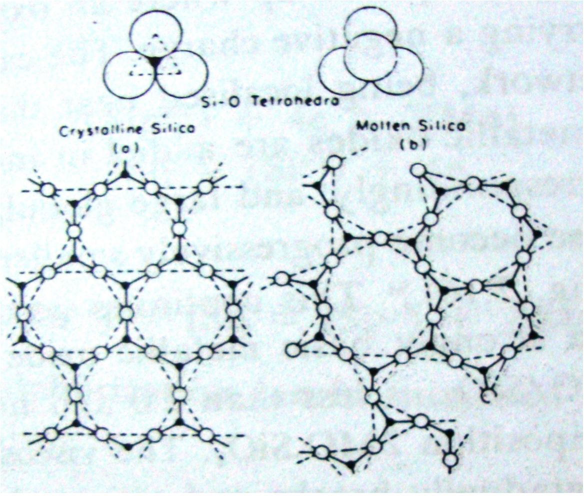


Fig. 4-Schematic representation of the silicate tetrahedron and crystalline and molten silica. The oxygen and silicon atoms are shown white and black respectively.

The (SiO_4) group, which is regarded as individual tetrahedron with silicon at the centre and oxygen at the four corners, can be assumed to exist as ion in the complex silicates. Measurement of the energy of activation for electrical conductance and other results indicate that the addition of CaO, MgO or other metal oxides to molten silica results in the breakdown of the three dimensional silicon-oxygen network into silicate ions. The driving force for the breakdown process is the attraction between silicon and oxygen. This depends on their relative valancies and ionic radii. [9]

1.5.4. MARKET SOURCES

Blast furnace slag materials are generally available from slag processors located near iron production centers.

Cements containing ground granulated blast furnace slag are available from many producers of Portland cement or directly from ground granulated blast furnace slag cement manufacturers. AASHTO M240 describes three types of blended cements containing slag. They include Portland blast furnace slag cement (type IS), slag modified Portland cement (type I (SM)), and slag cement (type S). The primary distinction among the three types is the percentage of slag they contain. Slag cement may contain Portland cement or hydrated lime (or both) while the other two are blends of Portland cement and slag only.

1.5.5. SLAG COMPOSITION

Slag typically makes up 20% (by mass) of iron production, so it's processing and reuse plays an important role in the operation of the iron and steel industry. Different forms of slag product are produced depending on the method used to cool the molten material emanating from the blast furnace. The elemental composition is a key factor determining process control. It is also central in assessing the suitability of different types of slag for specific applications. Although the relative amounts vary, the principal constituents of all blast furnace slags are silica, alumina, calcium and magnesium (reported as oxides). Minor elements include manganese, iron and sulphur compounds as well as trace quantities of several other elements. The chemistry usually has a narrow ratio of basic to acid components. Calcium and magnesium content, reported as equivalent oxides, normally results in a 1.25 to 1.55 basicity ratio.

The total basic elements, reported as equivalent CaO plus MgO divided by silica results in slag chemistry such as:

- CaO - 38%
- MgO - 10%
- SiO_2 - 36%

with minor elements such as:

- Iron Oxide (FeO &Fe_2O_3) - <1%
- Sulfur(S) - 1%
- Alumina (Al_2O_3) - 6-12%

Table-I depicts the typical chemical composition of blast furnace slag. The chemical compositions shown are in general applicable to all types of slag. The data presented in Table-I suggest that the chemical composition of blast furnace slag produced in North America has remained relatively consistent over the years.

Table-I: Typical composition of blast furnace slag [10]

Constituent	Percent							
	1949[a.]		1957[a.]		1968[a.]		1985[a.]	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Calcium Oxide (CaO)	41	34-48	41	31-47	39	32-44	39	34-43
Silicon Dioxide (SiO_2)	36	31-45	36	31-44	36	32-40	36	27-38
Aluminum Oxide (Al_2O_3)	13	10-17	13	8-18	12	8-20	10	7-12
Magnesium Oxide (MgO)	7	1-15	7	2-16	11	2-19	12	7-15
Iron (FeO or Fe_2O_3)	0.5	0.1-1.0	0.5	0.2-0.9	0.4	0.2-0.9	0.5	0.2-1.6
Manganese Oxide (MnO)	0.8	0.1-1.4	0.8	0.2-2.3	0.5	0.2-2.0	0.44	0.15-0.76
Sulfur (S)	1.5	0.9-2.3	1.6	0.7-2.3	1.4	0.6-2.3	1.4	1.0-1.9
a. Data source is the National Slag Association data: 1949 (22 sources); 1957 (29 sources); 1968 (30 sources) and 1985 (18 sources).								

1.5.6. SLAG VISCOSITY

In order that a blast furnace slag is practicable and most effective, it must be a completely homogenous liquid at the operating temperatures. It must be also have sufficient fluidity so that it can run out of the hearth freely without any loss of production time.

In blast furnace, formation of slag and the mineralogical transformation that the slag undergoes during descend of burden inside the furnace; influence the quality of hot metal. It is known that the components of slag namely silica and alumina increase the viscosity whereas the presence of calcium oxide reduces the viscosity. The melting zone of slag determines the cohesive zone of blast furnace and hence the fluidity and melting characteristics of slag play a major role in determining the blast furnace productivity. Initially iron rich slag is formed and thereafter due to assimilation of CaO and MgO from flux, the composition of slag varies. As the slag trickles down, it assimilates silica and alumina of ash, generated from combustion of coke. The process of trickling down depends on viscosity of slag, which further is governed by the composition and temperature of the melt.

Viscous behavior of blast furnace (BF) slags plays an important role that affects operation efficiency since the flow pattern of molten slags has a significant influence on gas permeability, heat transfer, and the reduction of SiO_2 and FeO. Since the reduction of iron ores and the formation of slags with coke/coal ash proceed in the BF, basicity (CaO/SiO_2) and FeO content in slags continuously change from the composition of initial sintered ore. Because the slags do not fully assimilate with ash in the bosh region of the blast furnace, they exhibit relatively high CaO/SiO2 (C/S) ratios of about C/S=1.4–1.6 and 5–20 percent FeO, which is compared with C/S_1.2 and FeO $\leq$ 0.2 mass% in tapped blast furnace slags. A relatively high basicity of slag in the bosh region is one of the main causes of slag formation problems.

The slag fluidity in a blast furnace affects softening-melting behavior in a cohesive zone, permeability in the lower part of a furnace due to liquid hold-up in a dripping zone, liquid flow in a furnace hearth, and the ability of the drainage slag by a taphole. The slag fluidity is affected by temperature and composition, with the latter influenced by ore gangue minerals and ash materials of coke and pulverized coal. CaO/SiO_2 in the slag, even in slag compositions, is adjusted in Japan to a range of 1.2 to 1.3 in concentration by an auxiliary material in terms of fluidity and desulfurization ability. The Al_2O_3 concentration in the slag is considered to be a factor that degrades the slag fluidity, which is semi-empirically set in Japan at the upper limit of about 15 to 16% in order to avoid the accumulation of the iron slag and the deterioration of permeability in the lower part of the furnace.

1.5.7. FLOW CHARACTERISTICS OF SLAG

High temperature microscope is used to determine flow characteristics of slag sample. It has got four characteristics temperatures to be studied:

- Initial deformation temperature (IDT)
- Softening temperature (ST)
- Hemispherical temperature (HT)
- Flow temperature (FT)

The followings are defined as per German Industrial Standards 51730.

1.5.7.1. INITIAL DEFORMATION TEMPERATURE (IDT)

Initial deformation temperature is the temperature at which the first rounding up of the edges of the cube-shaped sample specimen takes place. In fact this is the temperature at which the first sign of the change in shape appears. Rheologically this temperature symbolizes the surface stickiness of the slag.

1.5.7.2. SOFTENING TEMPERATURE (ST)

It is the temperature at which the outline of the shape of the sample starts changing and is reported as the temperature at which the sample shrinks by one division or the temperature at which the distortion of the sample starts. Rheologically this temp symbolizes the start of plastic distortion.

1.5.7.3. HEMISPHERICAL TEMPERATURE (HT)

It is the temperature at which the sample has fused down to hemispherical shape and is measured as the temp at which the height of the sample is equal to the half of its base length. This is defined as the fusion point or the melting point in germen industrial standards 51730. Rheologically this temperature symbolizes the sluggish flow of the slag.

1.5.7.4. FLOW TEMPERATURE (FT)

It is the temperature at which the sample liquidities and is reported as the temperature at which the height of the sample is equal to one-third of the height that it had at HT (hemispherical temperature). Though some books reported as the temperature at which the height becomes one-third of the initial height. The former is more accurate and is universally accepted. Rheologically this temperature symbolizes the liquid mobility of the slag.

CHAPTER 2

LITERATURE SURVEY

2. LITERATURE SURVEY

- **Y.S. LEE, J.R. KIM, S.H. YI, and D.J. MIN** [11] studied viscous behaviour of CaO-SiO_2-Al_2O_3-MgO-FeO slag. The viscosities of the CaO-SiO_2-Al_2O_3-MgO-FeO slags were measured under conditions of C/S=1.15–1.6, 10–13 percent Al_2O_3, 5–10 percent MgO and 5–20 percent FeO. They found that the viscosity of the BF type slag decreased by increasing the FeO content at a fixed basicity (CaO/SiO_2) of slags. Slag viscosity at low FeO (<7.5 percent FeO) exhibited a minimum value by increasing MgO content in slag. The addition of MgO does not affect the viscosity at FeO≥ 7.5 percent, while a minimum value is observed at about 7 percent MgO with 5 percent FeO.

  Viscosity decreased with increasing slag basicity up to 1.3 while it increased as slag basicity increased from 1.3 to 1.5. Therefore, they proposed that, with increasing the slag basicity, the driving force for the decreases of slag viscosity would be an increase in depolymerization of silicate network at C/S≤ 1.3, while the driving force for the increase of slag viscosity at C/S>1.3 is an increase in the chemical potential of solid compounds such as dicalcium silicate.

  The tests carried out by some Japanese companies have shown that flux Injection could decrease Si content of hot metal. A low level of Si content also means less amount of SiO_2 reduced to Si-fewer variations of Si content in hot metal and of slag basicity as well.

- **Kohei Sunahara, Kaoru Nakano, Masahiko Hoshi, Takanobu Inada, Shusaku Komatsu and Takaiku Yamamoto** [12] studied the effect of high Al_2O_3 slag on the blast furnace operations. They found that the slag drainage phenomenon in the furnace hearth is a fluidization phenomenon dominated by viscosity. The slag drainage rate decreases as the slag viscosity increases. Thus, to maintain slag drainage under high Al_2O_3, for instance, an increase of the MgO concentration in the slag is effective. Also, in this experiment range, the effects of the slag crystallization temperature on the slag drainage rate are relatively small in comparison to the effects of viscosity.

  The pressure drop in the dripping zone increases as the Al_2O_3 concentration in the slag increases. Even if the CaO/SiO_2 increases, the pressure drop in the dripping zone increases. The pressure drop is mainly caused by the effect of wettability as a result of the slag static hold-up, and little due to the effects of dripping slag viscosity and crystallization temperature. In the high Al_2O_3 concentration slag, to suppress the increase of the pressure drop in the dripping zone, it is effective that the decrease of the hold-up by the decrease of CaO/SiO_2.

The permeabile resistance in the cohesive zone is subject to Al_2O_3 concentration due to the permeable resistance index KS of the sintered ore at high temperature. The permeable resistance increases as the Al_2O_3 concentration in the ore increases. For instance, the increase of permeable resistance can be suppressed by an increase of MgO in the ore. As a result, in order to properly maintain slag drainage and permeability, they determined that the blast furnace design that increases MgO in the slag and decreases CaO/SiO_2 in the slag is effective.

- **J.-Y. JIA, C.-G. BAI, G.-B. QIU, D.-F. CHEN and Y. XU** [13] studied the Calculation models on the viscosity of $CaO\text{-}SiO_2\text{-}TiO_2$ slag system. The mass action concentration calculation model and viscosity calculation model are established, according to the coexistence theory of slag structure and document value under different temperatures and compositions for the $CaO\text{-}SiO_2\text{-}TiO_2$ ternary slag system. Calculated data is consistent with literature values.

  - With increasing TiO_2 per cent in slag, the mass action concentration increases. It is in agreement with practice.
  - With increasing TiO_2 per cent in slag, viscosity of slag decreases.
  - Temperature is a key to viscosity. If the temperature rises, viscosity decreases, and running quality is good.

- **Li ZHANG, Linnan ZHANG, Mingyu WANG, Guangqiang and Zhitong** [14] studied Dynamic Oxidation of the Ti-bearing Blast Furnace Slag. They arrived at the following conclusions:

  - The oxidation of (Ti_2O_3), TiC, TiN, Fe and (FeO) in the slag not only release a large amount of heat which causes the slag temperature increasing, but also decrease the slag viscosity.
  - The decrease of the slag viscosity, the increase of the slag temperature and air agitation promote the coalescence, growth and drop of the metallic Fe droplets in the slag. Most of metallic Fe droplets settle at the bottom of the slag pot, and the metallic Fe content in the slag decreases from 2.50 to 0.07%.
  - As oxidizing time approaches 12 min, the precipitation and growth of the perovskite phase rapidly increase, and the slag changes from the melt to a mixture of the melt and crystalline and the melting point of the slag rapidly increases, these effects cause the viscosity of the slag oxidized for 12 min rapidly increased.

- Bart J. P. Buhre, Gregory J. Browning, Rajender P. Gupta, and Terry F. Wall [15] studied the measurement of the Viscosity of Coal-Derived Slag Using Thermomechanical Analysis. A method for the determination of slag viscosity using Thermomechanical Analysis (TMA) has been developed, using a new flat ram assembly design. The low-temperature TMA experiments have suggested that many experiments are required to obtain a good estimate of the viscosity. At high temperatures, the technique shows good agreement with results obtained with the high temperature rotating bob viscometer for two out of four slags. However, the TMA apparatus under predicted the viscosities of the other two slags, for which several suggestions have been made. The limitations of the TMA technique, in comparison with the rotating bob viscometer, are as follows:

- Less-accurate results are obtained. Although the results show good agreement between the two techniques, the viscometer produces more-reliable and repeatable experimental results.
- The viscosity can only be determined at one temperature per test, as opposed to multiple temperatures in the rotating bob viscometer.
- The test must be performed above the liquidus temperature of the slag. This requires the use of thermodynamic packages such as FACTSage16 to assess the temperatures at which the viscosity of a particular slag can be determined.
- The results of the TMA test seem to be dependent on the slag used; the viscosities of some slags were measured correctly, whereas others showed an underestimation of the viscosity. Currently, no suggestions can be made for slag selection.

- The main advantages of the technique are as follows:

  - It is cost-effective. The TMA experiments require less (consumable) molybdenum per sample. It is important to note in this context is that the TMA experiments are relatively simple and the operator does not require extensive training.
  - It is rapid. Less than 3 h are required to complete a measurement.
  - It has small sample requirements. Measurements are performed on a small amount of sample.
  - It does not require calibration standards. No calibration standards are used to generate the apparatus constants; the viscosity is determined by a theory that requires only the measured dimensions of the sample assembly.
  - It can be used in a variety of environments. Although all measurements in this study were performed under argon atmospheres, the technique has the potential to be used in the oxidizing and reducing atmospheres of practical interest (with the appropriate material used for sample assembly construction).

- **Guozhuo Gong, Shufeng Ye, Yajun Tian, Yanbin Cui, and Yunfa Chen** [16] studied characterization of Blast Furnace Slag-$Ca(OH)_2$ Sorbents for Flue Gas Desulfurization. A series of sorbents for SO_2 from flue gas have been prepared from $Ca(OH)_2$ and BFS using a factorial experiment method. It was found that the activities of the sorbents prepared were higher than $Ca(OH)_2$ alone due to the formation of calcium silicate hydrates, which were mainly C-S-H(I). When the weight ratio of BFS/HL varied between 1/9 and 3/7, the SO_2 capture was independent of the specific surface area, and the SO_2 capture of the sorbents was equal to that of raw material $Ca(OH)_2$. When the weight ratio of BFS/HL varied between 7/3 and 9/1, the SO_2 capture was seen to increase linearly with the increase of specific surface area. Among the preparation variables and within the ranges investigated, the most significant variable for the specific surface area of the BFS/HL sorbent was the weight ratio of BFS/HL, and the best value was 9/1. The next two were hydration time (t) and ratio of water/solid (W/S), and their optimal levels were 10 h and 25/1, respectively. The last process variable studied was slurring temperature. The preferred temperature was 60 □C, but it was not necessary to control the temperature accurately, especially in industrial applications.

- **Chiung-Fang Liu and Shin-Min Shih** [17] studied the Kinetics of the Reaction of Iron Blast Furnace Slag/Hydrated Lime Sorbents with SO_2 at Low Temperatures: effects of the presence of CO_2, O_2, and NOx. The presence of CO_2, O_2, and NOx with SO_2 in gas phase at their typical concentrations in the flue gas had slight effects on the sulfation of BFS/HL sorbents, if O_2 and NOx were not present simultaneously. The reaction kinetics, being affected mainly by the relative humidity, can be described by the surface coverage model and the model equations derived previously for the reaction under the gas mixtures containing SO_2, H_2O, and N_2 only. When O_2 and NOx were present simultaneously, the sulfation of sorbents was greatly enhanced and a great amount of sulfate was formed in addition to sulfite. The surface coverage model is still valid in this case, but the model equations obtained show a more marked effect of relative humidity and negligible effects of SO_2 concentration and temperature. The presence of H_2O, CO_2, O_2, and NOx in the flue gas has positive effects on the SO_2 capture in the lowtemperature dry and semidry FGD processes which use BFS/ HL as the sorbent. The model equations obtained in this work are applicable to describe the kinetics of the sulfation of BFS/ HL sorbents in the FGD processes either with an upstream NOx removal unit or without.

- **Kiichi NARITA, Shin-ichi INABA, Masakata SHIMIZU, Arata YAMAGUCHI, Isao KOBAYASHI and Ken-ichi OKIMOTO** [18] studied the Burden and Gas Distribution considering Blast Furnace Aerodynamics. The behavior of charged burden has been studied aerodynamically by a model furnace, particularly concerning the formation of a central coke column. The column volume varied depending on the permeability of charged ore and the charging sequence. The change of gas velocity in the central part at the time of ore charging has been analyzed considering the permeability and piling profile of ore. The presence of a central coke column decreased the pressure drop in the furnace. It seems that a central coke column is formed in the practical blast furnace.

- **Yasuji kawai** [19] studied on the viscosities of molten slags and on the viscosities of CaO-SiO_2-Al_2O_3-MgO slags. Synthetic CaO-SiO_2-MgO and CaO-SiO_2-Al_2O_3-MgO (upto about 10% MgO) slags were melted in a graphite crucible in a high frequency induction furnace and the viscosities were determined by measuring the rotating speed of a graphite rod dipped in the molten slags. When MgO was added to CaO-SiO_2 slags, the viscosities decreases wit increasing amount of MgO up to about 20%, beyond which, however, it increased. The region of low viscosity was greater than that in CaO-SiO_2-Al_2O_3 slag. When MgO was added to CaO-SiO_2-Al_2O_3 slags, the viscosity decreased, moreover, changed in viscosity caused by the changing of slag composition at constant temperature became small, though these beneficial effects of MgO were less noticeable than those reported by previous investigators. To reduce the viscosity of high Al_2O_3 slags, the addition of MgO up to about 10% seemed to be insufficient. Viscosities of various slags which contain 10% MgO are shown in **Table II**.

Table II: Comparison of the effect of MgO on the viscosities of various slags.

Composition (%)				Viscosity(poise)	
CaO	SiO_2	Al_2O_3	MgO	1600 °C	1500 °C
40	50	10	-	8	20
36	45	9	10	3	8
40	50	-	10	3	9
40	40	10	10	2	5
30	50	10	10	10	20

In comparing the influence of MgO on the viscosities of various slags it is important to notice which component of slags is reduced in place of MgO added. It is essential condition to reduce the contents of SiO_2 and Al_2O_3 for obtaining low viscosity slags. MgO has nearly the same or a little less influence in reducing the viscosity of slags comparing with that of CaO and this suggests that abilities of basic oxides to reduce the viscosity of slags are in a close connection with the basicity of oxides.

- The microstructure of the burden is defined by the reduction degree, gangue, flux additions, phases, particle size, and distribution. According to **Barnaba** [20] and **Bakker** [21], the dependence of the softening temperature on the reduction degree occurs mostly due to the retention of the slag in the particle's core. On the other hand, **Borider** [22, 23] and **Ritz *et al*.** [24] attribute this to the reduction of the amount of FeO. Bonder found that the metallic iron content had an effect on the softening and melting temperatures of both olivine fluxed and acid pellets, but not on the basic pellets. For acid pellets reduced before the experiment, **Clixby** [25] found a dependence of the melting temperature on the reduction degree. In the experiments performed by **Khaki *et al.*** [26], the pellets were reduced during the softening and melting experiment. Different reduction degrees were obtained by varying the pellets' porosity. The melt formation temperature decreased with the rise in the reduction degree, while the dripping temperature increased. This may be due to the increase in pore size and also that the reduction degree was lower than 50 pct when liquid started to form in the pellet.

- The effect of reduction on the softening and melting of a MgO fluxed pellet was studied by **Sang-Ho Yi *et al.*** [27] In this case, a sample was reduced at 900 °C with a 70 pct N_2-CO mixture and then submitted to an industrial test. They found a reduction in the softening temperature and an increase in the melting temperature. The latter was due to the higher melting point of metallic iron when compared to FeO, while the former was attributed to the collapse of micropores. The samples with a larger fraction of small pellets (<12 mm) had better properties than those with larger samples. Since the diameter of the pellet has an influence on the reduction rate due to the mass transfer limitations, it indicates that higher reduction degrees are better.

- The influence of the reduction degree on the softening and melting phenomena occurs by two different mechanisms. The variation of the reduction degree will determine the volumetric fraction of metallic iron. Whereas the iron shell can hold the liquid slag, the dripping temperature may depend on its strength, which is a function of the iron layer thickness. Another effect of the reduction degree occurs by reducing the amount of FeO that can act as a slag former. In both cases, the higher the reduction degree, the higher should be the dripping start temperature. Several factors influence the reducibility of the burden material, which controls the reduction degree in the furnace. The addition of fluxing agents tends to increase the reducibility of the burden materials. [28] The pores will disappear at the beginning of softening. However, a coarser pore structure is fundamental for low-temperature reducibility. Nevertheless, coarse pores will tend to collapse sooner than fine ones. The heat generated in the firing of magnetite pellets may promote densification of the pellets. Also, in some cases the addition of lime may contribute to the reduction of the pore size, which along with the tendency for dissolution of FeO in the slag is deleterious to the reducibility. [29]

- The common gangue materials in the iron ore are silica and alumina. In the production of sinter, it is common to add flux materials such as MgO and CaO, to act as slag formers and to enhance sinterability. Pellets can be produced with or without flux additions. Although the addition of flux was initially done to enhance slag formation and reduce the amount of fines, it changes the softening and melting properties. The softening temperature increases with the reduction of the dolomite particle size, according to Bakker [21] and Barnaba [23], demonstrating that a fast dissolution of the flux agents into the slag improves the overall properties.

- The addition of both CaO and MgO increased the dripping temperature, as well as reduced the amount of nondripped material. This was attributed to the increase in reducibility and slag viscosity with basicity. In $CaO-SiO_2$ slags, the viscosity has a minimum around basicity of 1.8. This suggests that the increase in reducibility is the key factor in the increase in the dripping temperature by increasing the mechanical strength. Also, in another part of this work, it was seen that CaO substitutes for FeO as the basicity increases. This affects the viscosity and it will be discussed in part II of this series of article. Another beneficial effect of MgO was that it increases the viscosity of the slag at 1450 °C, but reduces it at higher temperatures, so that the slag drips together with the metal. According to **Bentell**, [29] the addition of MgO in lieu of CaO is beneficial because it will not form low melting point slags, especially at high MgO/SiO_2 ratios. Also, at high ratios, it is possible that the FeO matrix will melt earlier than the slag. **Yi *et al.*** [27] found that there is little effect of the addition of CaO or MgO on the softening temperature of the pellets they studied. However, they also found that the meltdown temperature increases by 1OO °C for the MgO-fluxed pellets in comparison to the acid and CaO-fluxed ones. The effect of the addition of MgO was studied from a theoretical viewpoint by Bakker. By analyzing the $CaO-MgO-FeO-SiO_2$ phase diagram, it was found that MgO increases the solidus temperature. The same approach was used in the $Al_2O_3-CaO-FeO-SiO_2$ system. In this case, it was concluded that the addition of Al_2O_3 reduced the solidus temperature. For a given Al_2O_3 or MgO content, the effect of the basicity on the solidus temperature was similar to that without the presence of the respective oxide. The effect of the alumina content in fluxed sinters was also studied by Barnaba. In this case, the effect was negligible in the dripping and softening temperatures. It is important to note that the alumina contents in the samples studied were lower than 3 pct.

- **G. Danloy , J. Mignon , R. Munnix , G. Dauwels , L. Bonte** [30] designed a Blast Furnace Model to Optimize the Burden Distribution. A mathematical model was developed which simulates the main phenomena involved in the blast furnace process at steady state. It was calibrated with experimental data obtained by vertical probing and by gas tracing at blast furnace B of Sidmar. The model results showed the strong influence of the burden distribution pattern on the gas distribution and on the different operating results such as the pressure drop, the productivity, the shape and position of the cohesive zone, the top gas temperature profile and the heat losses through the wall. As a consequence, it can be used to simulate and to forecast the influence of the burden distribution changes which are made by the operator. Therefore, it is a powerful tool to help him to choose the proper burden distribution pattern in function of the desired effect on the blast furnace results.

- **S.Z. Li, Jian Cheng, W.Q. Ma’s** [31] paper on a Method to Forecast the Cohesive Zone of Blast Furnace describes a method to forecast the cohesive zone of blast furnace whose shape is very important for the quality of iron and the efficiency of iron-making industry. This method builds a model that can be observed during the operation of iron making. The model considers that during the chemical reaction the ore, the coke and the gas abide by two equations: the equation of conservation of mass and the equation of heat conservation. Based on this presumption, by dividing the blast furnace into a series of homocentric circles in the height direction and resolving the equations in every homocentric circle with its own parameters, we can get the relationship between temperature and height of the inner blast furnace. And then, according to the fusibility character of the ore, we can forecast the shape and position of the cohesive zone. Finally, the paper visualizes the cohesive zone of blast furnace and discusses some results achieved through the application of such method to a real blast furnace.

- **Steven Wright, Ling Zhang, Shouyi Sun and Sharif Jahanshahi** [32] studied the viscosities of calcium ferrite slags and calcium alumino-silicate slags containing spinel particles. The viscosity of a calcium ferrite slag at 1280°C was determined with the addition of magnetite particles. The viscosities of slag/magnesite mixtures fit the Bingham model consistent with observations of Al2O3-CaO-MgO-SiO2 slags saturated with spinel particles. The dependence of the viscosity on the amount of solid addition could be described by the Einstein-Roscoe type equation.

$$\eta = \eta_o(1 - af)^{-n}$$

The effect of solids in the slags appeared to be much greater than expected from the theory. Fitting of the data with n fixed at 2.5, yielded a= -4.4, significantly larger than the theoretical a of 1.35 for uniform spheres. The effect of solid particles in calcium ferrite slags seems to be greater than on calcium alumino-silicate slags although effect of the shear thinning on the viscosity may be influencing the magnitude of the viscosity dependence. It would be worthwhile extending the measurements to larger shear rates.

CHAPTER 3

EXPERIMENTAL DETAILS

3. EXPERIMENTAL DETAILS

3.1. EXPERIMENTAL PROCEDURE

In the first stage, compositional details of Blast Furnace Slag samples were borrowed from the other group. The compositional details of these slags are presented in **Table III.** The charge history for the same produced is presented in **Table IV**. The flow characteristics data of Blast Furnace Slag was also borrowed for comparison with that obtained from synthetic slag. **Table V** shows the flow characteristics data of Blast Furnace slag.

Table III: Chemical Composition of Slag as obtained from SAIL, Rourkela

Blast Furnace	Cast No.	Chemical Composition of Slag as obtained from SAIL, Rourkela.					
		SiO_2 (%)	FeO (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	MnO (%)
I	21306	33.5	0.45	20.8	31.9	10.4	0.07
II	18582	33.7	0.47	20.6	31.9	10.5	0.08
III	7046	33.9	0.52	20.6	31.6	10.6	0.09
IV	11833	33.8	0.48	20.6	31.8	10.5	0.08

Table IV: Details of the charge generating the slag as obtained from SAIL, Rourkela

Blast Furnace	Cast No.	Amount of coke charged (Kg)	Amount of sinter charged (Kg)	Amount of ore charged (Kg)	Amount of flux charged (Kg)	Hot blast temp. (° C)	Hot metal temp. (° C)	Blast volume (Nm^3/hr)	Blast pressure (Kg/cm^2)
I	21306	808	1730	728	5	980	1428	81000	1.09
II	18582	723	1845	688	6	964	1430	90000	1.14
III	7046	780	1953	767	0	985	1422	88000	1.11
IV	11833	1201	2873	1154	5	985	1436	126000	1.49

Table V: Flow Characteristics of Blast Furnace slag samples as measured in the laboratory using the Hot-Stage microscope

Blast Furnace	Cast No.	Quarter No.	IDT (° C)	ST (° C)	HT (° C)	FT (° C)	Difference between ST and FT (° C)
I	21306	1	818	1212	1331	1372	160
		2	817	1217	1331	1373	156
II	18582	1	822	1198	1324	1367	169
		2	819	1193	1322	1408	215
III	7046	1	813	1218	1328	1398	180
		3	813	1215	1324	1383	168
IV	11833	1	814	1230	1326	1395	165
		3	822	1219	1323	1392	173

In the second stage, pure oxides (CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO) were heated in Hot Air Oven to remove the moistures. A powder mixture of weight 10 grams was made by mixing the oxides in the given proportion:

CaO- 34.5%, **SiO_2-** 33%**,** **Al_2O_3-** 21.5%**,** **Fe_2O_3-** 0.5%**,** **MgO-** 10.5%

Similarly 2 more sets were prepared and the three sets altogether were mixed in the machine with agate as the medium. The same procedure was repeated nine more times to make a mixture of oxides of weight 300 grams. A small weight of the above mixture was heated to about 1600°C and then quenched to prepare the required synthetic slag. A photograph of the slag made is shown in **Fig. 5**. The synthetic slag sample was then ground in planetary ball mill. The mill was rotated at a speed of 200 rpm for twenty five minutes. The medium was zirconia balls (ten in number of three different sizes for better interaction with the slag particles). A cone was made with the sample and then it was divided into four quarters. A small cube was made from each quarter. It was then heated in the heating microscope to measure the flow characteristics which is presented in **Table VI**.

Table VI: Flow Characteristics of Synthetic Slag as measured in the laboratory using the Hot-Stage microscope

Quarter No.	IDT (° C)	ST (° C)	HT (° C)	FT (° C)
1	817	877	1245	1394
3	819	877	1239	1386

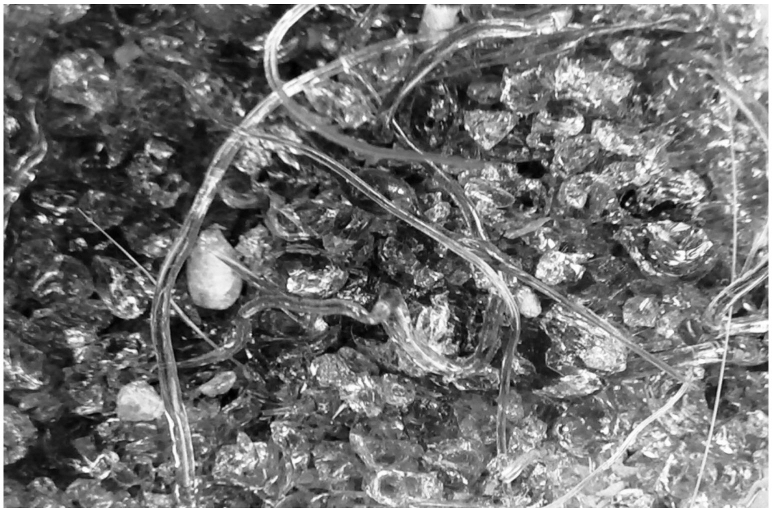


Fig. 5-Synthetic slag prepared in the laboratory

In the third stage, all the four blast furnace slag samples along with the synthetic slag sample was sent to DISIR, Rajgangpur for slag analysis where the composition of slag was also determined. The compositional details of these slags are presented in **Table VII.** All the slag samples were then heated to 1500°C followed by slow cooling. The mineralogical phases present in the slag samples were determined by XRD analysis.

Table VII: Chemical Composition of Slag as obtained from DISIR, Rajgangpur

Blast Furnace	Cast No.	Chemical Composition of Slag as obtained from DISIR, Rajgangpur					
		SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	TiO_2 (%)
I	21306	39.48	-	20.89	34.39	5.23	-
II	18582	34.97	0.73	19.31	34.39	9.8	0.6
III	7046	33.9	0.17	25.31	33.01	7.53	-
IV	11833	26.99	0.27	30.98	33.94	7.85	-

Finally, depending upon the major traces present in the samples and melting temperature of the same, related phase diagrams were found out. With the help of these phase diagrams, an attempt was made to vary the composition of slag in order to reduce the difference between ST and FT.

3.2. EXPERIMENTAL APPARATUS

3.2.1. HEATING MICROSCOPE

The Heating Microscope method is adopted for recording the characteristic temperatures. A picture of the Leitz heating microscope is shown in **Fig. 6**. Schematic diagram of the instrument is presented in **Fig. 7**. A detailed description of the instrument and its working principles is presented elsewhere [33].The sample, in the form of a 3 mm cube, is heated in an electric furnace in the microscope assembly. The shape change of the sample as a result of heating is photographed by a camera. A grid-division which is simultaneously photographed with the sample and the temperature to which the sample is being heated facilitate identification of the four characteristic temperatures. The four temperatures are reported as follows by following the German Industrial Standard 51730.

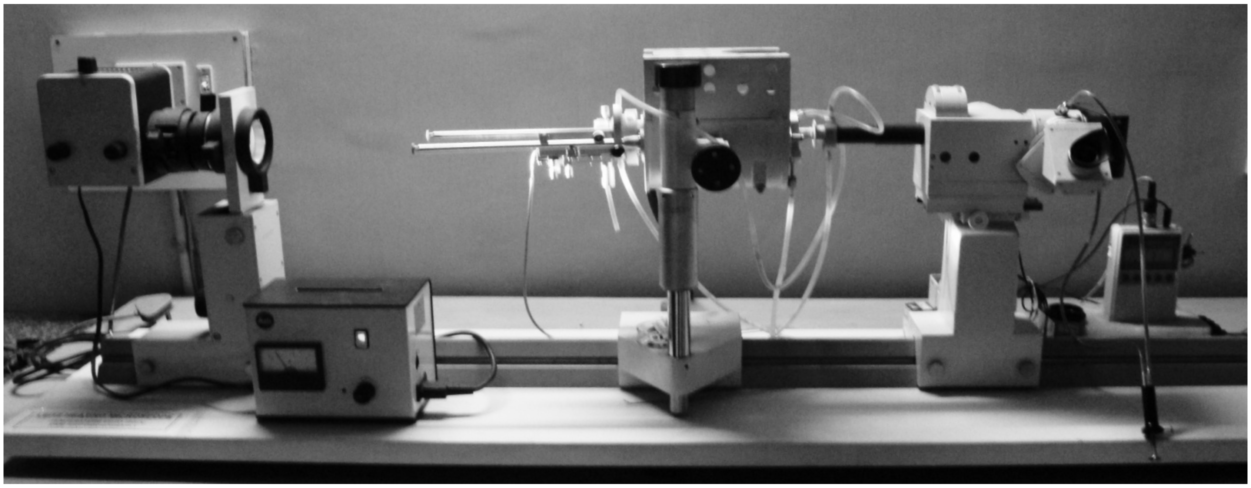
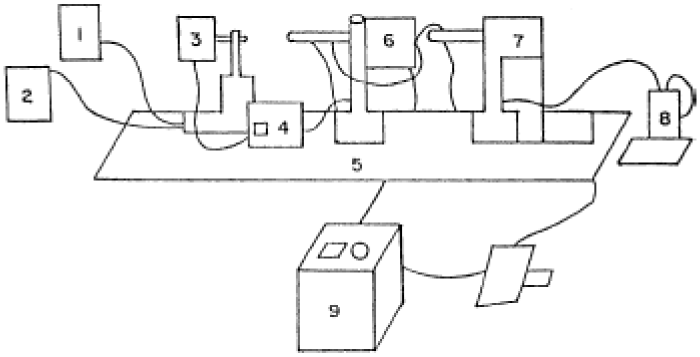


Fig. 6-Pictorial view of Leitz heating microscope



1. Cooling water tank
2. Cooling water recirculating tank

3. Light source
4. Regulating transformer for light source
5. Optical bench
6. High temperature electrical furnace with specimen carriage
7. Observation and photo microscope
8. Digital thermometer
9. Regulating transformer for high temperature electrical furnace

Fig. 7-A schematic diagram of the heating microscope

Two random samples are collected per slag for examinations. The average of the two readings is reported in case the two differ by not more than 50°C. In case the difference is more than 50°C fresh samples are drawn and the experiment is repeated. [4]

3.2.2. PLANETARY BALL MILL

Ball mills, also known as centrifugal or planetary mills, are devices used to rapidly grind materials to colloidal fineness (approximately 1 micron and below) by developing high grinding energy via centrifugal and/or planetary action.

An example of a four station planetary mill available through the Gilson Company is shown in **Fig. 8**. To grind a sample in this device, we have reduced the particle size to less than 10 mm, using a mortar and pestle if necessary. The material is placed in one of the bowls (shown in the lower right) and then several balls (shown in a tray at the bottom) are added. Samples can be run wet or dry. A cover is placed on the bowl and then the bowl is mounted in the machine. In the picture below, one bowl has been fastened down and the other has not yet been secured. Once the bowls are mounted and secured, the cover is lowered and the machine can be operated.

Each bowl sits on an independent rotatable platform, and the entire assembly of four bowls is also rotated in a direction opposite to the direction of the bowl platform rotation. This action is a lot like the "teacup and saucer" rides commonly found in amusement parks.

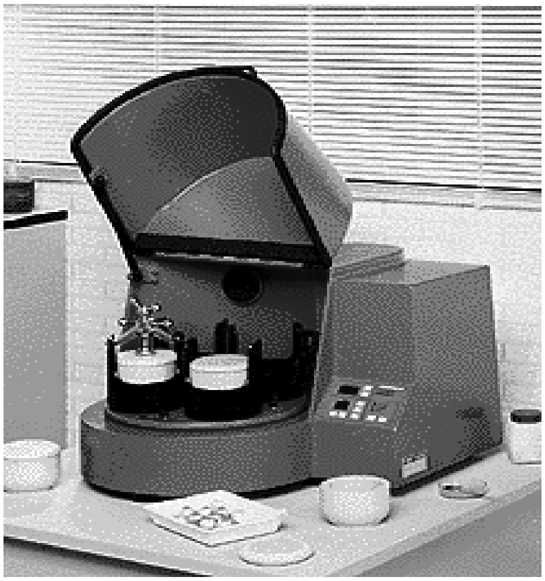


Fig. 8- A four station planetary mill

In planetary action, centrifugal forces alternately add and subtract. The grinding balls roll halfway around the bowls and then are thrown across the bowls, impacting on the opposite walls at high speed as shown in **Fig. 9**. Grinding is further intensified by interaction of the balls and sample. Planetary action gives up to 20 g acceleration and reduces the grinding time to about 2/3 of a simple centrifugal mill (one that simply spins around).

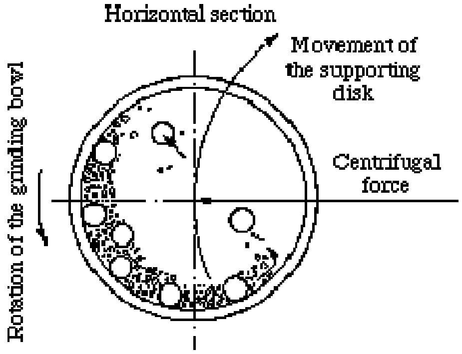


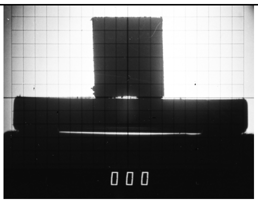
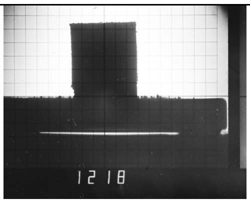
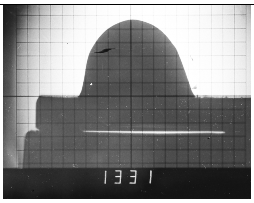
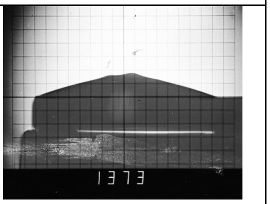
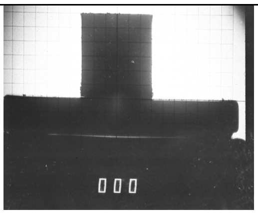
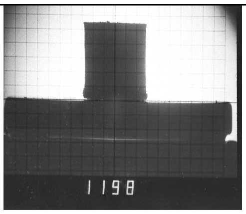
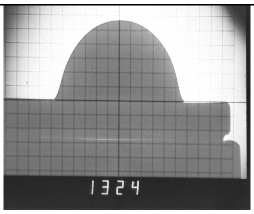
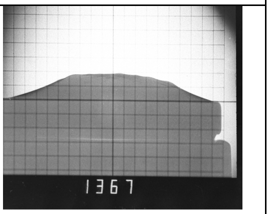
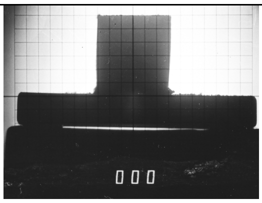
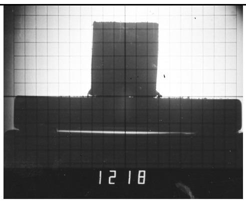
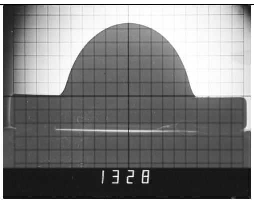
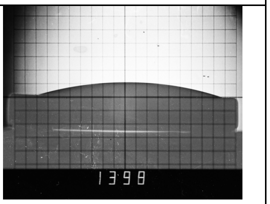
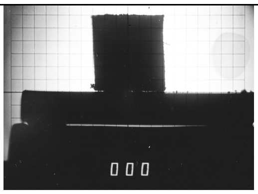
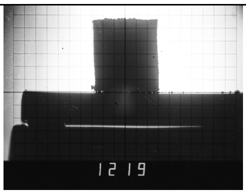
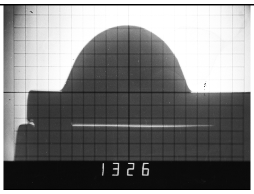
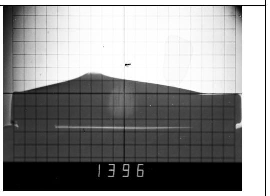
Fig. 9-Mechanism inside the ball mill

Grinding media are available in agate, sintered corundum, tungsten carbide, tempered chrome steel, stainless steel, zirconium oxide, and polyamide plastic. The exact type of bowl and balls that are used depend on the type of material being ground. For example, very hard samples might require tungsten carbide balls in steel bowls. For typical use, agate is a good choice. As with any method of grinding, cross contamination of the sample with the grinding unit material can be a complication. [34]

3.3. EXPERIMENTAL RESULTS AND DISCUSSION

3.3.1. *Flow characteristics measurement*

The flow characteristics of all the slag samples were measured in the heating microscope. The main aim was to determine softening temperature (ST) and flow temperature (FT) of the slag samples. We have borrowed the flow characteristics data of the Blast Furnace Slag in order to compare it with that of synthetic slag. ST, FT was also compared with variation in slag composition. Finally, we can get idea of the relevant phase diagrams from where an attempt was made to get a slag composition with a less difference between FT and ST. The micro-photographs of slag samples examined are presented in **Fig. 10**.

Sample	Original shape of the sample	ST (°C)	HT (°C)	FT(°C)
Blast Furnace I				
Blast Furnace II				
Blast Furnace III				
Blast Furnace IV				

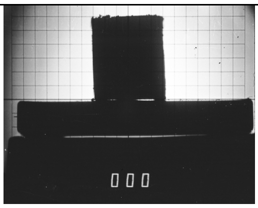
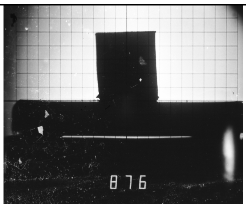
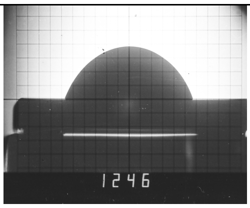
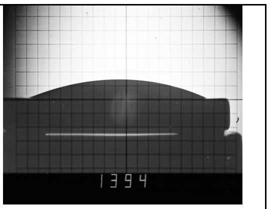
Synthetic slag				

Fig. 10-Micro photographs illustrating the characteristic temperatures of slag samples.

3.3.1.1. *Variation of ST, FT with wt % $Al_2O_3$and MgO*

From the chemical composition of slag as obtained from DISIR, Rajgangpur we tried to compare ST, FT with wt% of slag composition, basically with wt% Al_2O_3 and MgO. Relationship between ST, FT and wt% Al_2O_3 is presented in **Fig. 11** and that with MgO in Fig. 12.

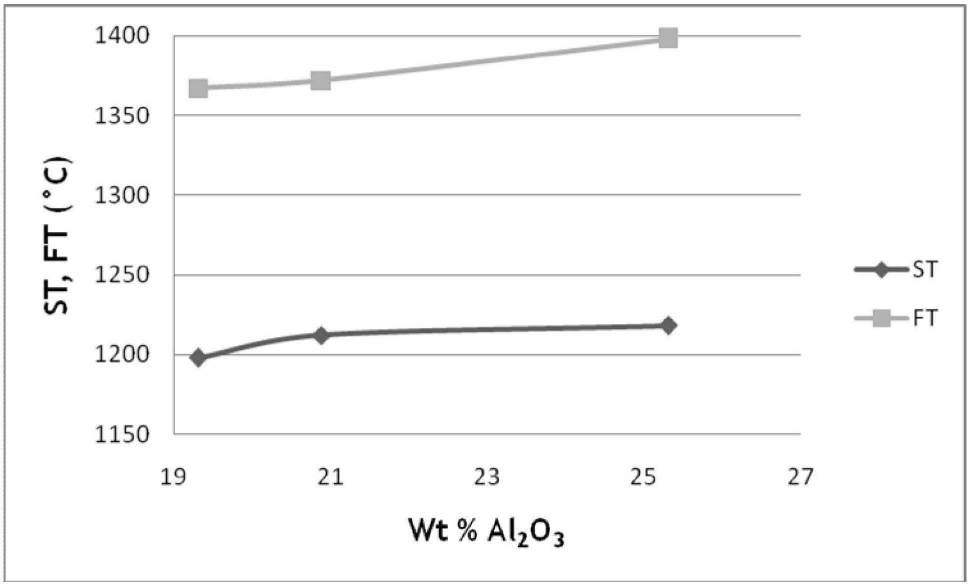


Fig. 11-Relationship between ST, FT and wt % Al_2O_3.

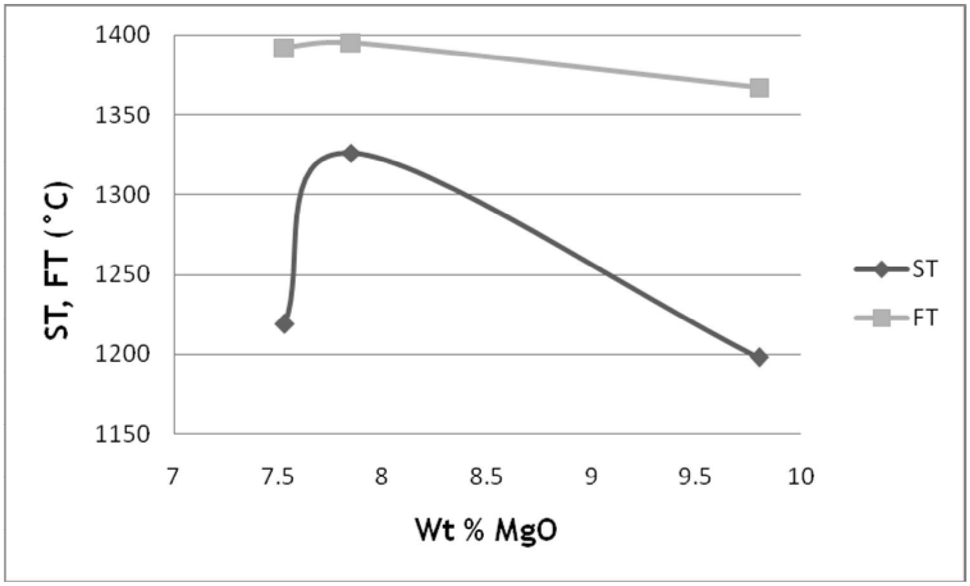


Fig. 12-Relationship between ST, FT and wt % MgO.

The blast furnace slags in addition to having Al_2O_3 and CaO as major constituents also contain other oxides like SiO_2, MgO, Na_2O, FeO, etc. Thus it is necessary to investigate how these oxides influence the liquidus temperature of the slag. To begin with Al_2O_3, there is hardly any difference with ST and FT only. But, when we see the difference between ST and FT, the plot shows that the difference is small in case of 20.89% Al_2O_3 while for other values it increases. So, ideally this composition should be suitable to obtain the desired slag. However, there are some minor phases which must be taken into consideration before arriving at any conclusion. We can easily see that in **Fig. 12**, the difference between ST and FT is small at around 7.85 % MgO while for other values of MgO content, the same increases. Hence, we conclude that so far as lowering of cohesive zone is concerned; Al_2O_3 content around 20.89% and MgO content around 7.85 % is beneficial. However, further investigations may have to be carried out at various other values of the Al_2O_3 and MgO before reaching at any decisive conclusion.

3.3.1.2. *Comparison of ST, FT data with that of Blast Furnace Slag*

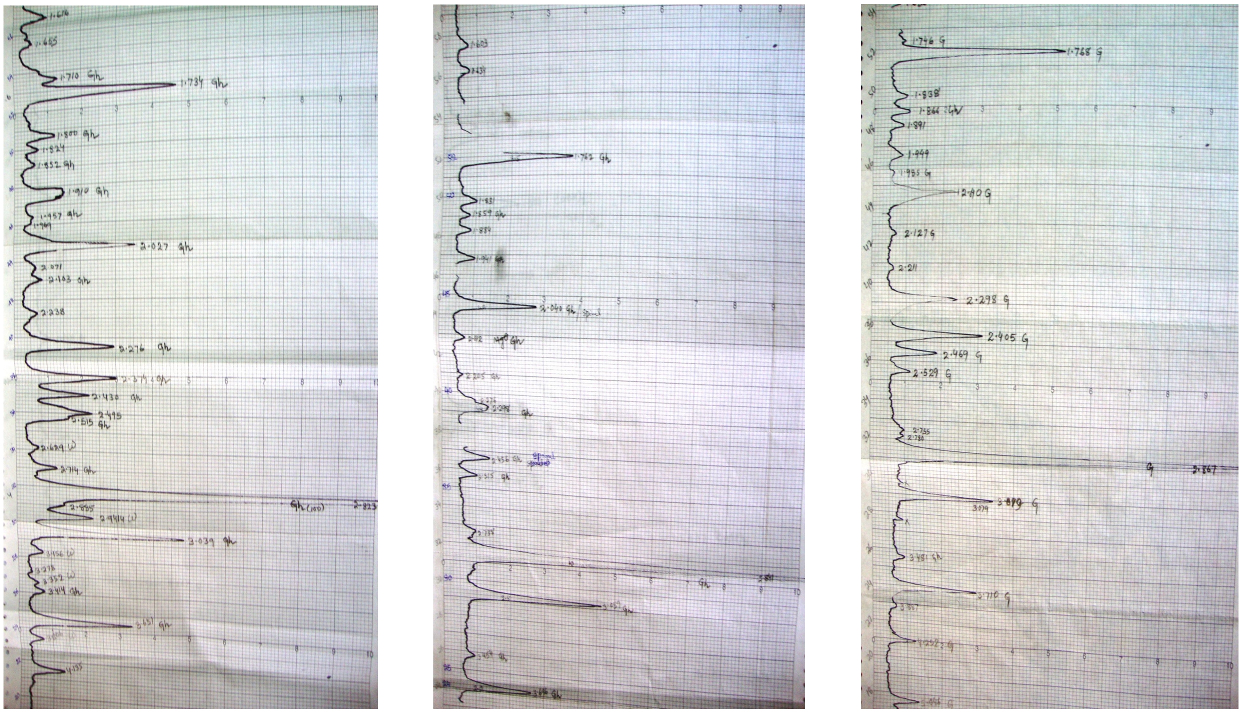
When comparing ST, FT data of synthetic slag with that of Blast furnace slag we observe that there is a slightly higher difference between ST and FT in case of synthetic slag. This may be due to presence of many minor phases present in the slag which may react and disturb the flow characteristics for which we need to study the XRD analysis. From XRD, we came to know the mineralogical phases present in the slag and those found in major traces are responsible for changes in ST, FT.

3.3.2. *XRD and Microscopic Analysis*

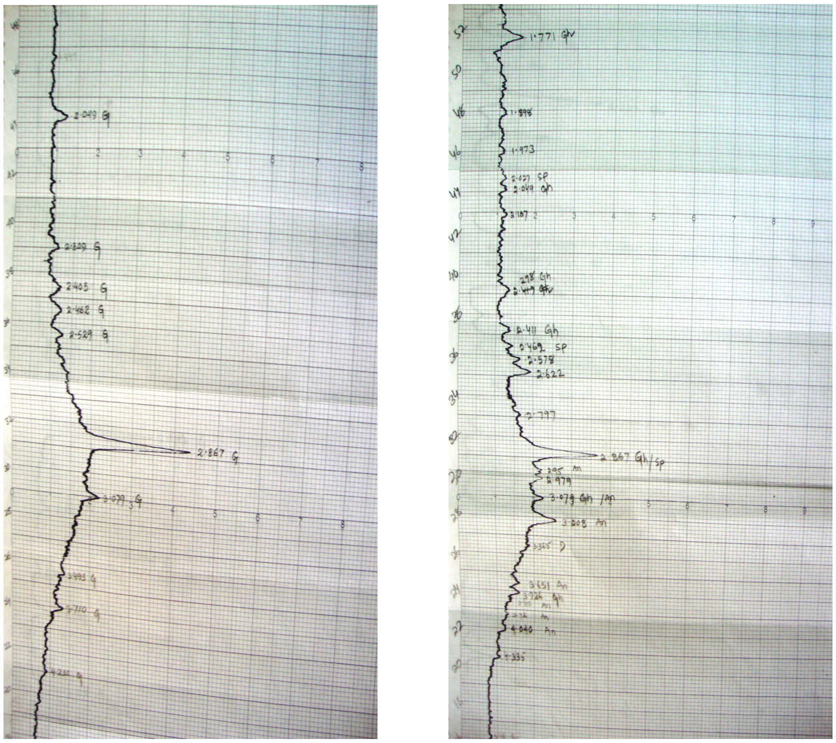
XRD analysis was done to get the mineralogical phases present in the sample. Slag was first heated to 1500 °C for one hour followed by slow cooling. The purpose of this was to convert the slag to crystalline form. Then XRD and microscopic analysis were done. Both the XRD and microscopic results are presented in **Table VIII** whereas XRD graphs are presented in **Fig. 13**.

Table VIII: XRD and Microscopic results of slag samples as obtained from DISIR, Rajgangpur

Sample	Traces obtained from XRD results	Microscopic result		
		Crystalline (%)	Glass (%)	Opaque (%)
BF I	Gehlenite, Anorthite, Spinel	93.0	6.9	0.1(Trace)
BF II	Monticellite, Gehlenite, Anorthite, Spinel	93.4	6.5	0.1(Trace)
BF III	Monticellite, Gehlenite, Anorthite, Spinel	92.0	7.9	0.1(Trace)
BF IV	Gehlenite, Anorthite, Spinel	91.4	8.5	0.1(Trace)
Synthetic slag	Gehlenite, Anorthite, Spinel	91.6	8.3	0.1(Trace)



(a) (b) (c)



(d) (e)

Fig. 13- XRD plots showing traces of mineralogical phases in case of (a) BF I (b) BF II (c) BF III (d) BF IV (e) Synthetic Slag. In all cases, Gehlenite was found to be the major phase. However, some traces of Anorthite and Spinel were also present.

From the XRD results we get the major traces of phases present in the slag sample. However, this may not be the actual path traced. But it is only the phases which bring about change in the melting point. So, our main aim was to find out the phases and not on the actual path of phase formation. Gehlenite ($Ca_2Al_2SiO_7$) was found to be the major phase in all slag samples. This crystalline phase was also being verified in the SEM micrographs as shown in **Fig. 14**. Keeping this in view, we study the related phase diagrams to find a suitable composition which will ensure decrease in the difference between ST and FT. We can play with in and around this composition because we never know which phases are responsible for lowering the difference between ST and FT. Therefore, further investigations may have to be carried out before reaching at any decisive conclusion.

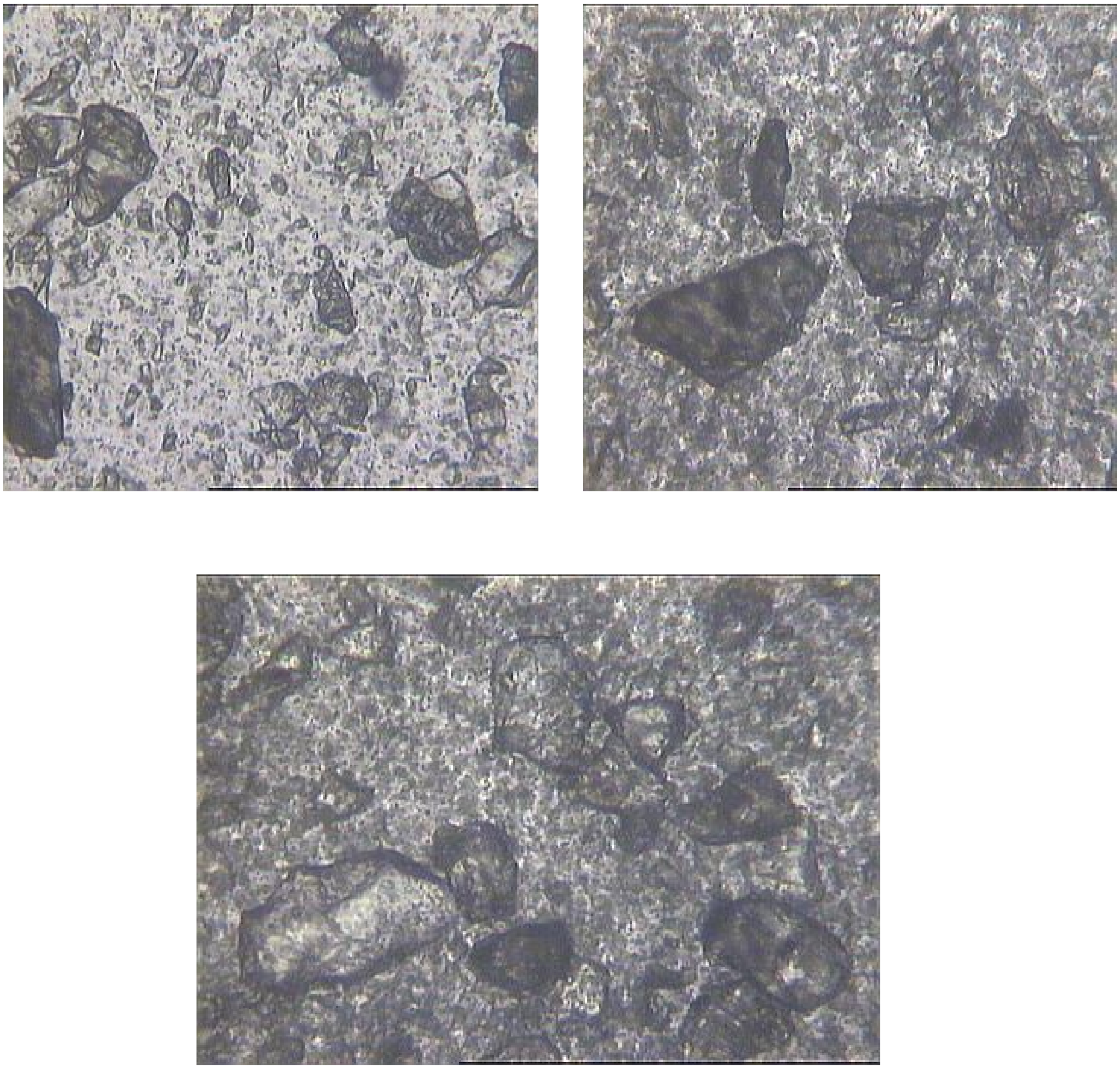


Fig. 14-SEM micrographs (magnification 100X) showing that the crystalline phase is Gehlenite

3.3.3. *Phase Diagram Study*

From XRD analysis we got Gehlenite, Anorthite and Spinel as the major traces. However, Gehlenite-Anorthite sytem was not found. So we studied the Anorthite-Spinel system as shown in **Fig. 15**.

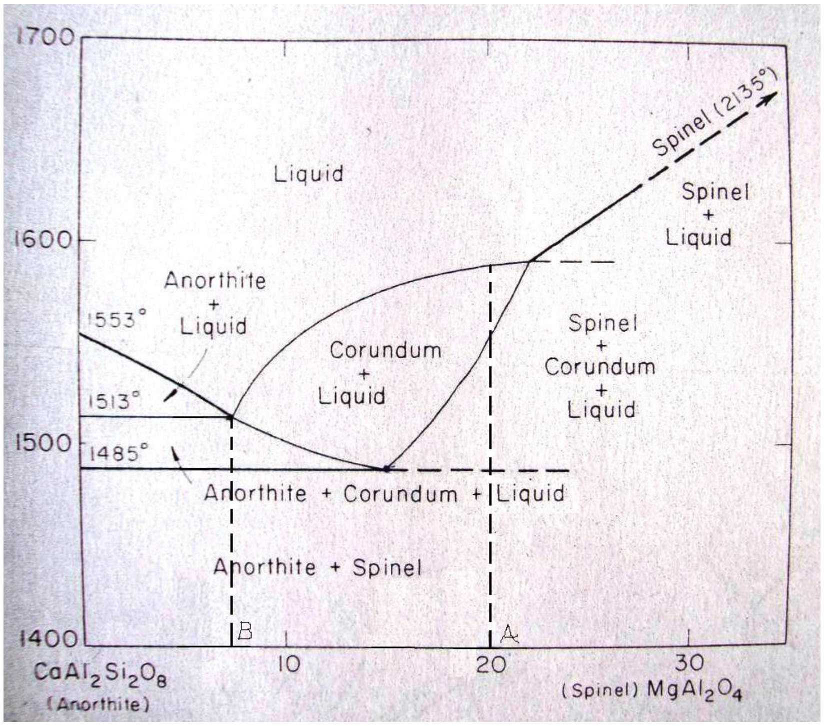


Fig. 15-System $CaAl_2Si_2O_8$-$MgAl_2O_4$. Heavy lines indicate binary relationships

From phase diagram we see that melting point of Anorthite ($CaAl_2Si_2O_8$) is 1553°C while that of Spinel ($MgAl_2O_4$) is 2135°C. Suppose we choose a point A in the diagram corresponding to 20% Spinel and 80% Anorthite composition. At this composition we get the onset of melting temperature at 1485 °C but flow temperature at around 1580 °C. However our aim is to lower the difference between ST and FT. For this we shifted the composition towards the point B in phase diagram. The composition at point B is 8% Spinel and 92% Anorthite. At this composition we can see that onset of melting temperature is same, i.e., 1485 °C whereas flow temperature is reduced to 1513 °C. This also resulted in lowering the difference between ST and FT. Thus by playing in and around 8% Spinel composition we can get our desired result. In other words, by changing the amounts of MgO and Al_2O_3 so that Spinel composition is around 8%, we can get our desired result. A decrease in the difference between onset of melting temperature and flow temperature will ensure lowering of cohesive zone in the blast furnace. As a result less Si pick up in the hot metal is achieved.

CHAPTER 4

CONCLUSION

4. CONCLUSION

We hope that as a result of our work, we can throw light on the generation of slag of given composition through appropriate selection of raw materials which will ensure lowering of coke consumption and greater control of metal composition by control of slag-metal reaction. By experimentation with synthetic slag and data borrowed from experimentation with Blast Furnace slag, we arrived at the following conclusion:

- Addition of MgO content around 7.53 % is beneficial for a narrow cohesive zone down the furnace (as obtained from experimentation with Blast Furnace Slag).
- Addition of 20.89% Al_2O_3 is suitable for obtaining a slag with less difference between ST and FT (as obtained from experimentation with Blast Furnace Slag).
- The study of the phase diagram gave us the idea of the slag composition which would ensure lowering of cohesive zone. We can play with the composition of slag by preparing a number of synthetic slags in the laboratory and then measure their flow characteristics.

The future prospect of this project is to play with the composition which will lower the cohesive zone by preparing synthetic slag and melting it to study the flow characteristics. This will be compared with that of Blast Furnace slags obtained from different steel plants of India. Flow characteristics as a function of oxides like Al_2O_3, CaO, MgO, etc will be investigated. Depending upon the phases and flow characteristics determined, related phase diagrams will be found out. From the study of the phase diagrams we can arrive at a number of compositions with a lower difference between ST and FT and hence suitable addition can be done to alter the measured characteristics for a narrow cohesive zone lower down the furnace. On the basis of final slag, burden distribution will be predicted. There is a plan to introduce the predicted burden in a real low shaft furnace. The project will also include burdening the furnace with sinter/pellet with different size ranges of ore and flux. Finally, we will arrive at a slag composition which will have some industrial importance.

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